

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 696 761 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

14.02.1996 Bulletin 1996/07

(51) Int. Cl.⁶: G03F 7/038, G03F 7/033

(21) Application number: 95202170.7

(22) Date of filing: 09.08.1995

(84) Designated Contracting States:

BE DE ES FR GB IT NL

(30) Priority: 10.08.1994 EP 94202298

(71) Applicant: SHELL INTERNATIONALE RESEARCH

MAATSCHAPPIJ B.V.

NL-2596 HR Den Haag (NL)

(72) Inventors:

• Mayenez, Catherine

B-1348 Ottignies Louvain-la-Neuve (BE)

• Muyldermans, Xavier

B-1348 Ottignies Louvain-la-Neuve (BE)

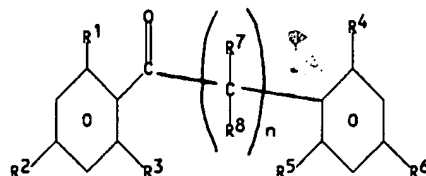
(54) Flexographic printing plates from photocurable elastomer compositions

(57) Flexographic printing plates, obtainable by exposing to UV irradiation of a photocurable polymer composition, comprising at least

(a) 100 parts by weight (pbw) of a block copolymer containing at least three poly(conjugated diene) blocks and at least one block selected from poly(monovinylaromatic) blocks, and having a branched or radial structure, of the general formula $[AB]_p[C]_qX$ wherein each A represents a predominantly poly(monovinyl- aromatic) block, each B and C represent a predominantly poly(conjugated diene) block, p and q each represent an integer of 1 or higher and the sum of which is in the range of from 3 to 20 and preferably from 4 to 8, and wherein X represents the residue of a polyfunctional coupling agent, any present poly(butadiene) blocks B and C in which having a 1,2-polymerization degree of from 20% to 75% of the originally present butadiene and each of the poly(conjugated diene) blocks having an apparent molecular weight in the range of from 30,000 to 150,000 and the blocks B and C representing from 65 to 93% by weight of the total block copolymer weight;

(b) from 0.1 to 5 pbw of at least one photoinitiator, selected from the group consisting of:

(1) a benzophenone of the general formula (I)



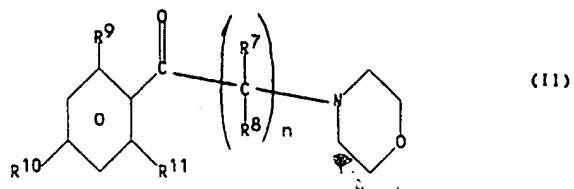
(I)

wherein R¹ to R⁶ independently represent hydrogen or an alkyl group having from 1 to 4 carbon atoms, preferably methyl, and wherein R⁷ and/or R⁸ have the same meaning as R¹ to R⁶ or represent in addition alkoxy of 1 to 4 carbon atoms and wherein n has a value of 0, 1 or 2 optionally in combination with at least one tertiary amine;

EP 0 696 761 A1

Eng E9 of
JP 8-69107A

(2) a compound of the general formula II



wherein R⁹, R¹⁰ and R¹¹ each may represent hydrogen, alkyl of 1 to 4 carbon atoms, or an alkylthio having 1 to 4 carbon atoms, while at least one of substituents R⁹, R¹⁰ and R¹¹ represents alkylthio.
(3) and mixtures of (1) and (2).

Description

The present invention relates to flexographic printing plates derived from photocurable elastomer compositions, and more in particular from photocurable elastomer compositions comprising at least one block copolymer, derived from at least a poly(monovinylaromatic) block and a poly(conjugated diene) block, and at least one photoinitiator.

Said printing plates, also called flexo plates, are especially useful for commercial printing and packaging of diverse products such as frozen food bags, orange juice cartons, potato chips bags, boxes and envelopes.

Photocurable polymer compositions are well known in the art for forming printing plates and other radiation sensitive articles.

In the field of flexographic printing plates the plates typically comprise a support and a photosensitive layer prepared from the photocurable composition.

Additional layers on the plate include slip and release films to protect the photosensitive surface. Prior to processing the plate, the additional layers are removed and the photosensitive layer is exposed to radiation in an imagewise fashion. The unexposed areas of the layer are then removed in developer baths.

Photosensitive layers of photocurable compositions for the preparation of flexographic printing plates, often have been described in a widely diverging array of types, such as those in German patent application Nos. 2138582, 2223803, 2364873, 2610206, 2631837, 2720228, 2815678; US patents Nos. 2,760,863, 2,948,611, 3,024,180, 3,674,486, 3,798,035 and 3,951,657, 4,023,973, 4,762,892, and 5,250,389; European patent application Nos. 0,219,795, 0,422,488, 0,467,135, 0,553,662 and Japanese patent applications Nos. 59142538, 61098344, 63161443 and 63309568.

However, those photocurable polymer compositions as specified therein, have appeared to leave a need for further improvement to provide practically acceptable irradiation exposing times in combination with the relief depth as presently required by the printing industry in combination with a relatively low hardness and preferably without using any toxic ethylenic unsaturated compounds at all or only at very small not earlier used concentrations.

Moreover, there is still existing a need for further improvement of the total combination of relevant physical properties of such photocurable compositions for printing plates.

In addition to possessing an easily developable less dangerous photosensitive layer, a flexographic printing plate must be flexible enough to wrap around a printing cylinder, strong enough to withstand the rigors experienced during typical printing process, soft enough to facilitate ink transfer during printing process and resistant enough to the particular ink solvent to avoid blurring of the image. On the other hand it is important that the photosensitive layer of the printing plate be dimensionally stable during storage. Some compositions earlier proposed for making printing plates, have shown inferior stability properties, in that the compositions become tacky and pasty.

It will be appreciated that the achievement of an attractive balance of all these physical properties will be difficult.

As can be derived from e.g. European patent application no. 0525206, more recently attempts to develop an improved combination of desired properties of photocurable polymer compositions and flexographic printing plates derived therefrom, were directed to the use of thermoplastic block copolymers, comprising

(1) at least one predominantly monovinyl substituted aromatic hydrocarbon polymer block and at least one predominantly conjugated dienepolymer block, said block copolymer having a monovinyl substituted aromatic hydrocarbon content (A) of 10 to 35 wt%, and said conjugated diene having a vinyl content (V) of 20 to 50%, and the sum of (A) + (V) being in the range of from 40% to 70%

(2) and 1 to 20 wt%, based on the weight of the elastomer composition of an ethylenically unsaturated compound as a photocuring auxiliary; and

(3) 0, 1 to 3 wt% based on the weight of the elastomer composition, of a photopolymerization initiator

As component (2) was used a member selected from the group consisting of an acrylate a methacrylate, a maleimide or diesters of maleic acid or fumaric acid, which still represent a toxic and/or expensive auxiliary.

From European patent application no. 0543632 were known photocurable polymer compositions and flexographic printing plates derived therefrom, comprising random copolymers of various acrylates and conjugated dienes or triblock copolymers, comprising at least a polymer segment of a C₂-C₅-alkyl methacrylate or methacrylic acid and at least a polymer segment of a conjugated diene.

Accordingly, an object of the present invention is formed by an easily developable, photo cured flexographic printing plate, showing a decreased hardness and preferably without the use of toxic and/or expensive photocuring auxiliaries.

More in particular it is an object of the invention to prepare a solid photosensitive layer which is flexible, yet strong and durable, which has a relatively low hardness and can be obtained preferably without said additional photocurable auxiliaries.

It is also an object to prepare a solid photosensitive layer which, when cured in an imagewise pattern, results in a relief pattern layer which easily and clearly transfer ink in instances the layer is that of a flexible printing plate.

A particular object of the present invention is to provide flexographic printing plates from photocurable block copolymer containing compositions, which can be achieved by improved irradiation exposure times during the usual manufacture of flexographic printing plates, without any deterioration of the other properties of the photocurable compositions during the manufacture of the relief form and with more attractive hardness.

More in particular these compositions aimed at should provide an attractive visual appreciation system for a pictorial irradiated form before the development step by changing the absorption behaviour. More preferably these compositions aimed at should be substantially free or almost free of the usually applied additional crosslinking monomer.

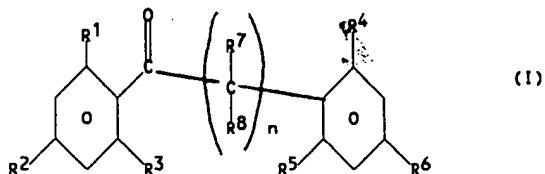
As a result of extensive research and experimentation such a flexographic printing plates aimed at have now been surprisingly found.

Accordingly one aspect of the present invention is relating to flexographic printing plates obtainable by exposing to UV irradiation a photocurable elastomer composition, comprising at least

(a) 100 parts by weight (pbw) of a block copolymer containing at least three poly(conjugated diene) blocks and at least one block selected from poly(monovinylaromatic) block, and having a branched or radial structure, of the general formula $[AB]_p [C]_q X$; wherein each A represents a predominantly poly(monovinyl- aromatic) block, B and C represent a predominantly poly(conjugated diene) and preferably a predominantly poly(butadiene), block p and q each represent an integer of 1 or higher and the sum of which is in the range of from 3 to 20 and preferably from 4 to 8, and wherein X represents the residue of a polyfunctional coupling agent, any present poly(butadiene) blocks B and C in which having a 1,2-polymerization degree of from 20% to 75% of the originally present butadiene; and each of the poly(conjugated diene) blocks having an apparent molecular weight in the range of from 30,000 to 150,000, and the blocks B and C representing from 65 to 93% by weight of the total block copolymer weight;

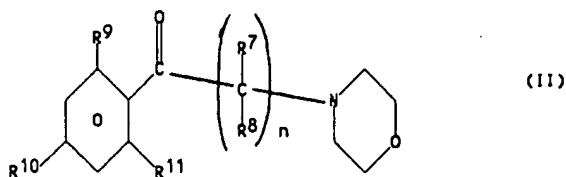
(b) from 0.1 to 5 pbw of at least one photoinitiator, selected from the group consisting of:

(1) a benzophenone of the general formula (I)



wherein R^1 to R^6 independently represent hydrogen or an alkyl group having from 1 to 4 carbon atoms, preferably methyl, and wherein R^7 and/or R^8 have the same meaning as R^1 to R^6 or represent in addition alkoxy of 1 to 4 carbon atoms and wherein n has a value of 0, 1 or 2, optionally in combination with at least one tertiary amine;

(2) a compound of the general formula II



wherein R^9 , R^{10} and R^{11} each may represent hydrogen, alkyl of 1 to 4 carbon atoms, or an alkylthio having 1 to 4 carbon atoms, while at least one of substituents R^9 , R^{10} and R^{11} represents alkylthio.

(3) and mixtures of (1) and (2).

With the expression "apparent molecular weight" as used throughout the specification is meant the molecular weight as determined by Gel Permeation Chromatography using poly(styrene) calibration standards of different molecular weights.

It will be appreciated that the respective blocks A and/or B and/or C in the total block copolymer configuration may be composed of the same or different monomers. The blocks B and/or C may optionally be selectively hydrogenated partially, the remaining ethylenical unsaturation of the total ethylenical unsaturation being in the range from 50 to 20% of the original unsaturation.

With the term "predominantly" as used throughout the present specification is meant that the respective blocks may be constituted by a main monomer and a minor monomer, which may be structurally similar to the major monomer or may be structurally different from the main monomer and may occur in an amount of up to 10 wt% and preferably up to 5 wt%, relative to the total weight of comonomers of said block.

The monovinylaromatic monomer as major component in block A and optional minor component in blocks B and/or C may be selected from styrene, α -methylstyrene, o-methylstyrene, p-methylstyrene, p-tert-butylstyrene, 1,3-dimethylstyrene or mixtures thereof. Styrene is the most preferred monomer.

The conjugated diene to be used as major ingredient in blocks B and/or C is butadiene and/or isoprene which may be mixed with small amounts of 2,3-dimethyl 1,3-butadiene; 1,3-pentadiene 1,3-hexadiene or mixtures thereof, and of styrene, α -methylstyrene, o-methylstyrene, p-methylstyrene, p-tert-butylstyrene, 1,3-dimethylstyrene or mixtures thereof. However, pure 1,3 butadiene or pure isoprene for each blocks B and/or C are the most preferred monomers.

As preferred component (a) multi-armed block copolymers, containing pure poly(butadiene and/or isoprene) blocks, pure poly(styrene) blocks or combinations of said blocks are used.

The content of 1,2-polymerized conjugated diene in the B and C blocks of the block copolymer component (a) when poly(butadiene) is preferably in the range of from 35 to 65% and more preferably from 50 to 60%. The apparent molecular weight of each of the predominantly poly(conjugated diene) blocks is preferably in the range of from 40,000 to 120,000 and more preferably from 50,000 to 90,000.

Each of the predominantly poly(monovinylaromatic) blocks have an apparent molecular weight in the range of from 5000 to 50,000 and preferably in the range of from 7000 to 35,000 and more preferably of from 9,000 to 17,000.

According to a much preferred embodiment, radial block copolymers $(AB)_p(C)_qX$ are used wherein the weight average molecular weight of the blocks B and C are substantially the same.

The block copolymers to be used in the photocurable compositions as specified hereinbefore, can be prepared by methods known per se, such as disclosed in e.g. PCT application WO 93/24547; Polymer Preprints 26(1), 1985, p247-248, European patent applications Nos. 0298667 and 0314256.

Examples of suitable polyfunctional coupling agents can be $SiCl_4$, BTMSE, GPTS, DEAP, TMS, $Cl_3Si-(CH_2)_n-SiCl_3$, such as BTCSE, $(RO)_3Si-(CH_2)_n-Si(OR)_3$ such as BTMSE, $RCI_2Si-(CH_2)_n-SiCl_2R$, $Cl_3-SiSi-Cl_3$, $Cl_3Si-O-SiCl_3$; $RCI_2Si-(CH_2)_n-SiCl_2-(CH_2)_n-SiCl_2R$, $R-C(CH_2SiCl_3)_3$, $C(CH_2-SiCl_3)_4$ and the like.

It will be appreciated that the radial or branched block copolymers used as component (a) of the photocurable polymer composition will contain a minor amount of diblock or homopolymer, which formed the initially prepared constituting elements before coupling.

Examples of suitable compounds of category (1) are benzophenone, 2,4,6-trimethylbenzophenone, 4-methylbenzophenone, an eutectic mixture of 2,4,6-trimethylbenzophenone and 4-methylbenzophenone (ESACURE TZT) or 2,2-dimethoxy-1,2-diphenylethan-1-one (IRGACURE 651) (ESACURE and IRGACURE are trade marks). These compounds may be employed in combination with tertiary amines, such as e.g. UVECRYL 7100 (UVECRYL is a trade mark).

Category (2) embraces compounds such as e.g. 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropanone-1, commercially available as IRGACURE 907.

In a preferred embodiment of the present invention the photoinitiator is selected from the group consisting of (i) benzophenone or 2,2-dimethoxy-1,2-diphenylethan-1-one (IRGACURE 651), and (ii) 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropanone-1 (IRGACURE 907) or mixtures of one or both of these components with other members of groups (1) and (2).

Most preferred is the use of 2,2 dimethoxy-1,2-diphenylethan-1-one (IRGACURE 651) or 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropane (IRGACURE 907) as single photosensitizer.

The photoinitiator should be present in an amount of from 0.1 to 5 parts by weight per 100 parts by weight of block copolymer (phr) to ensure sufficient cross-linking upon exposure to UV irradiation. It is preferred that the photoinitiator is present in an amount of from 0.5 and 2 phr.

The UV irradiation used for cross-linking the block copolymer composition of the present invention in principle may be any UV source having an output spectra showing one or more peaks at wavelengths between 200 and 500 nanometer (nm) and preferably in the range from 230 to 450. Particularly suitable UV sources are Fusion bulb lamps (Fusion is a trade mark) having output maxima at 260-270 nm, 320 nm and 360 nm ("H" bulb), at 350-390 nm ("D" bulb) or at 400-430 nm ("V" bulb). Combinations of these Fusion bulb lamps may also be used. H and D bulb lamps are particularly useful, while a combination of D bulb and H bulb can also be suitably applied.

The exposure to UV irradiation may be performed by any known method. A suitable method for instance is exposing a sample either in a layer obtained from a hot melt or in a layer obtained by solvent coating to UV irradiation by exposure through a negative placed between the light source and the photosensitive surface underneath. If necessary, the exposure to irradiation may be repeated one or more times, e.g. by repeatedly irradiating the sample layer underneath the UV source in order to accomplish a sufficient curing, providing sharply contrasted printing pictures.

The photocurable and in particular UV curable block copolymer compositions according to the present invention can be suitably applied as hot melt or as solution in an organic solvent.

It will be appreciated that in addition to the two hereinbefore specified main ingredients the photocurable polymer compositions may comprise one or more of the following optional ingredients

- (c) 0.1-3 phr of an antioxidant/UV stabilizer,
- (d) 0-80 phr of a plasticizer,
- (e) 0-300 phr of an organic solvent relative to the weight of block copolymer.

If any plasticizer is used, it is used in an amount of from 20 to 60 phr.

Examples of a suitable solvent are methylisobutylketone, cyclohexane, or cyclopentane, methylethylketone, n-hexane, isopentane or mixtures thereof.

It will be appreciated that for most flexographic printing plate preparations, hot melt compositions will be preferably used and no solvent at all.

As component (c) any antioxidant commonly applied in block copolymer formulations, may be used in the present compositions.

Examples of such antioxidants/stabilizers are those marketed under the trademarks IRGANOX and SUMILIZER e.g. IRGANOX 1010 and TNPP and the like.

As component (d) can be suitably used, as plasticizer for the poly(conjugated diene) blocks if any, both naphthenic and paraffinic oils, or low molecular weight polybutylene or poly(butadiene) polymers. Examples of suitable plasticizers are SHELLFLEX 371 and 451 and TUFFLO 6204 (naphthenic oils), TUFFLO 6056 (paraffinic oil), and the low molecular polybutylenes HYVIS 200, NAPVIS 30 and NAPVIS D-10, (SHELLFLEX, TUFFLO, HYVIS and NAPVIS are trademarks).

Other useful plasticizers for poly (conjugated diene) blocks are REGALREZ 1018, ONDINA 68 or ONDINA G 33 and V-OIL 7047 (REGALREZ, ONDINA and V-OIL are trademarks).

Useful plasticizers for the poly (mono vinyl aromatic) blocks are selected from lower molecular weight polystyrene ($M_w < 3000$) and copolymers of styrene, α -methyl styrene and other vinyl aromatic monomers, such as ENDEX 160, KRISTALEX F85, KRISTALEX 5140, PICCOLASTIC A75 (ENDEX, KRISTALEX and PICCOLASTIC are trademarks).

Also reactive esters of ethylenically unsaturated acids can be used in small amounts as a plasticizer, which is compatible with the poly(monovinyl aromatic) blocks.

The photocurable block copolymer compositions may be applied on a carrier in the form of a hot melt composition or in a solution of an organic solvent.

It will be appreciated that both types of application forms form also aspects of the present invention. Another aspect of the invention is formed by cured compositions in the form of flexographic printing plates, obtained by exposing the applied composition layer to UV irradiation.

The photocurable compositions can be applied as layers of the desired thickness.

For example the layers of these compositions can be derived from solutions in suitable solvents or from hot melt compositions, by pouring an appropriate layer on the support. In alternative ways said layers can be prepared by hot pressing, extrusion and calendering.

The layer thickness may normally vary depending on the final application purpose; for photosensitive recording elements such as flexographic printing plates it can vary in the range of from 0.01 to 50 mm and preferably from 1 to 6.5 mm thickness.

As layer support for these photosensitive compositions can be used any flexible material such as foil from polyethylene-terephthalate, polybutylene terephthalate, having a sufficiently high elasticity modulus, which can be used as dimensionally stable transparent support material and which are resistant to washout solutions.

It may be desirable to protect the photosensitive surfaces from contamination by dirt and dust during storage before being exposed and washed. Such protection may be accomplished by application of a flexible protective cover sheet to the side of the photocurable composition opposite that of the support. In addition, the photocurable compositions can sometimes be tacky and in such case it may be desirable to apply a release film to the surface of the photosensitive layer before application of the cover sheet. The release film may consist of a thin flexible, developing solvent dispersible polymeric film placed in intimate contact on the surface of the photocurable composition. Such release films are well known in the art.

Photosensitive articles comprising a support having a solid layer or surface comprising the photocurable compositions of the present invention, e.g. solid flexographic printing plates, can be processed by well known techniques for imagewise exposure to actinic light. Exposure takes place through a transparent support layer to form a continuous cured undersurface of the layer and subsequently through a negative placed between the light source and the photosensitive top surface.

Exposure periods depend upon the intensity of the actinic light, thickness of the plate, and the depth of the relief desired on the printing plate. Exposure periods of from 1 second to 20 minutes are generally suitable. After exposures and removal of the negative, the unexposed areas of the photosensitive surface can be developed in washout solutions as herein described. Imaged plates made with the hereinbefore specified block copolymers may be washed with organic

solvents e.g. hexane or methylethylketone, optionally mixed with a lower alkanol such as methanol, ethanol, isopropanol or butanol.

It will be appreciated that the photocurable compositions⁵ and printing plates produced therewith are characterized by an attractive hardness in combination with other relevant physical properties as described below.

Shore A Hardness

Shore A hardness is similar to modulus in that a polymer with a high hardness value will not conform easily to the analog roll or substrate, and ink transfer will be poor. Values in the range of about 35-70° are deemed desirable for flexographic printing application.

Herein resilience were determined by ASTM D 2632-79; and Shore A hardness by ASTM D 2240.

It will be appreciated, that photocurable compositions according to the present invention surprisingly have been found to provide flexographic printing plates which have the required properties and in particular a relatively low hardness (even without plasticizer) by curing without the presence or in the presence of only small amounts of unsaturated monomers to have adapted the final hardness.

The invention is further illustrated by the following examples, however without restricting the scope of the invention to these specific embodiments.

(A) Photocurable compositions were prepared from 100 parts by weight of the block copolymers, derived from styrene and butadiene, specified in the table 1, 1 part by weight of the antioxidant IRGANOX 1010 and 2 parts by weight of the photoinitiator IRGACURE 651.

POLYMER CHARACTERISTICS

POLYMER (AB)p(C)q	A block mol wt% (GPC) (*1000)	AB block mol wt% (GPC) (*1000)	Average p	Average q	A (%w)	Vinyl content (%) in B and C
P1	10.7	71	2	2	12.7	54
P2	10.7	81	2	2	12.5	60.5
P3	10.7	62	2	4	10	56
P4	9.4	58	2	4	10	57
Comparative TR-1102	11	62	2	0	29	<5
P5	12	125	1.4	0	17	40

* Apparent GPC molecular weight based on Polystyrene calibration.

Formulation : polymer + monomers ** 97p

Photoinitiator : IRGACURE 651 2p (all examples
except example
7)

IRGACURE 907 2P (example 7)

Anti oxidant : IRGANOX 1010 1p

** 100%, 95%, 90% or 70% of polymer in the blend polymer-monomer
(Diethyl maleate)

Blend performed in toluene (100%)

Plates produced with a heated press at 140°C, 20 bars, 30 min.

Photocuring : Several passes at 2.5 m/min under a 300 W/inch
linear UV lamp covered by a elliptic mirror (American ultraviolet
co lamp 06C OF)

Results:

EXAMPLES							
Example	Polymer	Shore A hardness before curing	Thickness (mm)	Number of curing passes	Shore A hardness after curing	Gel content (%)	Swell ratio
1	P1 (100%)	28	2.5	10	39	84	9.8
2	P2 (100%)	30	3.0	10	53	94	7.5
3	P3 (100%)	16	2.1	5	31	91	12.1
				10	46	96	5.9
4	P3 (95)	16	2.0	5	32	92	11.4
				10	41	95	6.0
5	P3 (90%)	14	2.1	5	33	91	12.5
				10	39	95	5.6
6	P4 (100%)	17	2.2	10	39	96	7.7
7	P2 (100%)	29	3.0	10	47	90	12
Compar. 8	TR-1102 (100%)	69	2.2	10	70	85	17.4
Compar. 9	P5 (100%)	50	2.1	10	62	91	8.9

The Shore A hardness is measured after 3s.

The gel content (%) is expressed as the weight ratio of the dried extracted gel (after dissolution in toluene 100%) by the corresponding sample before dissolution.

The swelling ratio is expressed as the weight ratio of the swelled gel (in toluene 100%) by the corresponding dried gel (dried to constant weight under vacuum).

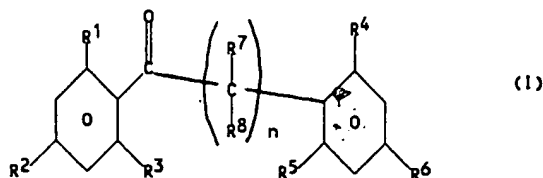
Claims

1. Flexographic printing plates, obtainable by exposing to UV irradiation a layer of a photocurable elastomer composition, comprising at least

(a) 100 parts by weight (pbw) of a block copolymer containing at least three poly(conjugated diene) blocks and at least one block selected from poly(monovinylaromatic) blocks, and having a branched or radial structure, of the general formula $[AB]_p[C]_qX$ wherein each A represents a predominantly poly(monovinylaromatic) block, each B and C represent a predominantly poly(conjugated diene) block, p and q each represent an integer of 1 or higher and the sum of which is in the range of from 3 to 20, and wherein X represents the residue of a polyfunctional coupling agent, any present poly(butadiene) blocks B and C in which having a 1,2-polymerization degree of from 20% to 75% of the originally present butadiene and each of the poly(conjugated diene) blocks having an apparent molecular weight in the range of from 30,000 to 150,000; and the blocks B and C representing from 65 to 93% by weight of the total block copolymer weight;

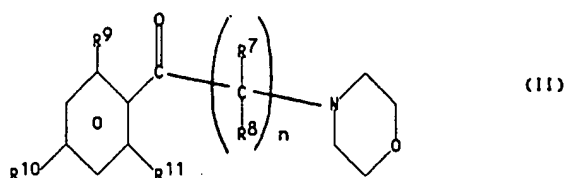
(b) from 0.1 to 5 pbw of at least one photoinitiator, selected from the group consisting of:

(1) a benzophenone of the general formula (I)



wherein R¹ to R⁶ independently represent hydrogen or an alkyl group having from 1 to 4 carbon atoms, preferably methyl, and wherein R⁷ and/or R⁸ have the same meaning as R¹ to R⁶ or represent in addition alkoxy of 1 to 4 carbon atoms and wherein n has a value of 0, 1 or 2, optionally in combination with at least one tertiary amine.

(2) a compound of formula II



wherein R⁹, R¹⁰ and R¹¹ each may represent hydrogen, alkyl of 1 to 4 carbon atoms, or an alkylthio having 1 to 4 carbon atoms, while at least one of the substituents R⁹, R¹⁰ and R¹¹ represent an alkylthio

(3) and mixtures of (1) and (2).

2. Flexographic printing plates according to claim 1, characterized in that component (a) of the photocurable composition is consisting of a multi-armed block copolymer, containing pure poly(styrene) blocks and pure poly(butadiene) and/or poly(isoprene) blocks or combinations of said blocks.
3. Flexographic printing plates according to claims 1 and 2 characterised in that the sum of p and q in the block copolymer component (a) is in the range from 4 to 8.
4. Flexographic printing plates according to claims 1-3, characterized in that the content of 1,2-polymerised conjugated diene in the total block copolymer component (a) is in the range of from 35 to 65%.
5. Flexographic printing plates according to claims 1-4, characterized in that the predominantly poly(monovinyl aromatic) blocks in component (a) of the photocurable composition have an apparent molecular weight in the range of from 9000 to 17,000.
6. Flexographic printing plates according to claims 1-5 characterized in that component (b) is comprising 2-methyl-1-[4-(methylthio)-phenyl]-2-morpholinopropanone-1 or 2,2-dimethoxy-1,2-diphenylethan-1-one.
7. Flexographic printing plates according to claims 1-6 characterized in that the photocurable compositions is applied in a layer of from 0.01 to 6.5 mm thickness on a layer support of a transparent flexible material.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 20 2170

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	<p>DATABASE WPI Section Ch, Week 8819 Derwent Publications Ltd., London, GB; Class A89, AN 88-128571 & JP-A-63 070 242 (NIPPON ZEON KK) , 30 March 1988 * abstract *</p>	1-7	<p>G03F7/038 G03F7/033</p>
A,D	<p>WO-A-93 24547 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 9 December 1993 * page 16, line 1 - line 17; claims 17-20 *</p>	1-7	<p>TECHNICAL FIELDS SEARCHED (Int.Cl.6)</p> <p>G03F</p>
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 22 November 1995	Examiner J.-M. DUPART
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons Δ : member of the same patent family, corresponding document</p>			

EPO FORM 1503 (3.8.92) (P/C01)